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Generalized product expansions for pair-correlated wavefunctions

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A correlated wavefunction in the form of a linear combination of generalized products is proposed for describing electron correlation in N-electron systems. The generalized product configurations are group functional products describing the correlated behavior of a pair of electrons in an N-2-electron independent particle sea. The linear expansion includes terms for all possible pairs and thus includes correlation effects for every pair of electrons. The structure of the wavefunction is given, the matrix elements of the Hamiltonian are determined, and some of the variational equations determining the optimal total wavefunction are discussed. The relation between second-order Nesbet–Bethe–Goldstone calculations and the pair at a time CI method of Sinanoğlu and the pair-correlated wavefunction developed here is discussed, and a method is given for obtaining a complete generalized product wavefunction from these type independent pair approximations.

I. INTRODUCTION

In recent years a large number of configuration interaction (CI) calculations have appeared for a variety of atomic and molecular systems. These calculations have provided a good deal of information as to the types of terms which are important for effectively introducing electron correlation into the wavefunction, and which electronic interactions are sensitive to the variation of one or more of the structural parameters of the system.

Based on these experiences a number of variational and perturbational approaches have been proposed which are designed to introduce the important terms in a simple fashion and at the same time exhibit the most important features of electron correlation. One type of approach consists of constructing the wavefunction based on a particular model such as the electron pair model.[1] This approach has seen a number of applications[2] and developments.[3] Another way of proceeding is to assume that the CI expansion has sufficiently converged after only the lowest order contributions have been included in the wavefunction. Both perturbation[4] and variational[5,6] methods have been proposed. A third way of proceeding is by describing electron correlation only for those electrons for which the correlated behavior depends strongly on one or another change in the structure of the system, viz., the internuclear distance in diatomic molecules.[7]

From most of these studies it has become clear that it is not necessary in most instances to consider the simultaneous correlations of all the electrons in a system, but that for most purposes it is sufficient to consider the interactions between only a few electrons at a time. This result has the important consequence that the determination of correlated wavefunctions is simplified and the computation time needed to calculate properties from such wavefunctions is reduced.

The question of what types of many-body terms must be included in the wavefunction and to what extent they must be optimized in order to give an adequate description of a certain class of properties for a variety of systems has been studied by several workers.[4,8] Two expansion methods have been useful for carrying out this study and for developing efficient procedures for determining correlated wavefunctions. These are the cluster expansion[9–11] and the generalized product of group functions[12] forms for expanding the wavefunction. While cluster expansion variational wavefunctions including all pair correlations have been previously proposed,[9,13–16] the generalized product approach has only been partially exploited.[17]

When an N-electron wavefunction is approximated by considering the correlations of subsets of all the electrons, the group function idea is formally introduced into the wavefunction, i.e., correlated and uncorrelated electrons. By expanding the wavefunction in terms of such group products a very compact expression for the total wavefunction is obtained and in addition the usual CI expansion coefficients split up into two or more distinct subgroups. Variationally optimal wavefunctions (with respect to a given subset of parameters) can then be determined with a concomitant reduction in the dimensionality of the energy matrix which must be evaluated and diagonalized.

For the pair-correlated wavefunction developed below the most obvious division leads to an $N(N-1)/2$-dimensional matrix which must be diagonalized. In the first section of the paper the relation between the cluster expansion and the generalized product forms of the wavefunction are discussed and some matrix element formulas between group

function products are given.[12] In the second section the detailed structure of the pair-correlated generalized product expansion is obtained, energy formulas and variational equations are derived, and the explicit forms of the matrix elements are given. Finally the relationship between the generalized product wavefunction and the independent electron pair method is discussed, and a method is given for obtaining the $N(N-1)/2$-dimensional energy matrix from that approximation.

II. FORMULATION IN TERMS OF GROUP FUNCTIONS

A. N-electron Wavefunction with p Electrons Correlated

Consider an approximate wavefunction which describes the correlation of a particular subgroup of p electrons of the total N-electron system. A cluster expansion for such a wavefunction can be obtained from the complete cluster expansion by eliminating all those clusters which contain electrons not belonging to the subset $(p)=i_1<i_2<\cdots<i_p$. One obtains an expansion of the form[9,10,18]

$$\Psi_{(p)}=\mathcal{A}\Big[\Phi_0+\sum_{(1)\subset(p)}\Phi_{(1)}+\sum_{(2)\subset(p)}\Phi_{(2)}+\cdots+\sum_{(q)\subset(p)}\Phi_{(q)}+\cdots+\Phi_{(p)}\Big], \tag{1}$$

where $\mathcal{A}$ is the complete antisymmetrizer and the summations run over the p-tuple. The $\Phi_{(q)}$ are functions which describe the correlation of a particular q-tuple of q electrons. Now assume a set of N orthonormal one-electron spin functions, $\{\phi_i\}_1^N$, and a set of cluster functions,[9-11] $\{f_{(q)}\}_1^p$, for describing the correlation of the 1, 2, $\cdots$, p particles. Then Φ_0 is the reference state and is given by the product

$$\Phi_0=\phi_1(1)\,\phi_2(2)\cdots\phi_N(N) \tag{2}$$

and

$$\begin{aligned}\Phi_{(q)}=&f_{(q)}(1,2,\cdots,q)\,\phi_1(q+1)\\&\times\phi_2(q+2)\cdots\phi_{i_1-1}(q+i_1-1)\,\phi_{i_1+1}(q+i_1)\\&\cdots\phi_{i_r-1}(q+i_q-r)\,\phi_{i_r+1}(q+i_q-r+1)\cdots\phi_N(N).\end{aligned} \tag{3}$$

Thus $\Phi_{(q)}$ is formed from Φ_0 by replacing the one-electron orbitals $\phi_{i_1}, \phi_{i_2}, \cdots, \phi_{i_q}$, by the arbitrary function $f_{(q)}$ which describes the correlation of the q-tuple (q).[10] Since each Φ is finally operated on by the antisymmetrizer the numbering of the coordinates is arbitrary and at most $\Phi_{(q)}$ must be multiplied by -1.[17]

From Eq. (3) it is seen that each term in $\Psi_{(p)}$ of Eq. (1) contains the common set of one-electron functions,

$$\phi_1,\ \phi_2,\cdots,\ \phi_{i_1-1},\ \phi_{i_1+1},\cdots,\ \phi_{i_p-1},\ \phi_{i_p+1},\cdots,\ \phi_N,$$

which can be factored out from each term in Eq. (1). One obtains

$$\Psi_{(p)}=\mathcal{A}\Big[\Big(\prod_{l=1}^{p}\phi_l+\sum_{(1)\subset(p)}f_{(1)}\prod_{l\neq(1)}^{p}\phi_l+\cdots+\sum_{(q)\subset(p)}f_{(q)}\prod_{l\neq(q)}\phi_l+\cdots+f_{(p)}\Big)\Big(\prod_{l\neq(p)}\phi_l\Big)\Big], \tag{4}$$

where the first term in parentheses runs over particles 1, $\cdots$, p and the second term runs over particles $p+1$, $\cdots$, N. Now write the complete antisymmetrizer as a product of partial antisymmetrizers,[19]

$$\begin{aligned}\mathcal{A}&=(N!)^{-1/2}\sum_Q(-1)^Q Q\\&=\left\{\binom{N}{p}^{-1/2}\sum_{Q'}(-1)^{Q'}Q'\right\}\left\{(p!)^{-1/2}\sum_{Q_p}(-1)^{Q_p}Q_p\right\}\\&\quad\times\left\{[(N-p)!]^{-1/2}\sum_Q(-1)^Q Q\right\}=\mathcal{A}'\mathcal{A}_p\mathcal{A}_{(N-p)},\end{aligned} \tag{5}$$

where $\mathcal{A}_p$ acts only on particles 1, $\cdots$, p in Eq. (4), $\mathcal{A}_{(N-p)}$ acts only on particles $p+1$, $\cdots$, N in Eq. (4), and $\mathcal{A}'$ interchanges particles between the two groups. With these definitions $\Psi_{(p)}$ can be written in generalized product[19] form, namely

$$\Psi_{(p)}=\mathcal{A}'[\Lambda_{(p)}\,\Delta_{(p)}]. \tag{6}$$

Equation (6) gives the generalized product equivalent of the cluster expansion of Eq. (1). From Eqs. (3) and (4) it is seen that $\Lambda_{(p)}$ describes all correlations of the subset (p) up to order p, whereas the function $\Delta_{(p)}$ is the antisymmetrized orbital product constructed from the set $\{\phi_i\}_1^N$ after the spin-orbitals $\phi_{i_1}, \phi_{i_2}, \cdots, \phi_{i_p}$ have been removed.

B. Matrix Elements between Group Function Products

For cluster functions of the type introduced in Eq. (3) it has been shown by Sinanoğlu[6,20] and Szasz[13] that strong orthogonality, in the sense

$$\int\bar{f}_{(p)}(1,2,\cdots,p)\,\Delta_{(q)}(1,2',\cdots,N'-q')\,d\tau_1=0, \tag{7}$$

where $\bar{f}$ is the complex conjugate of f, holds without loss of generality if (q) belongs to a finite subspace of the many-electron Hilbert space which is orthogonal to the subspace defined by $\phi_{i_1}, \phi_{i_2}, \cdots, \phi_{i_p}$. The group function $\Lambda_{(p)}$ is a linear combination of terms which are products of cluster functions and one-electron functions belonging to the group (p). Since the latter are also orthogonal to the functions in $\Delta_{(p)}$ the type of strong orthogonality given in Eq. (7) can be applied directly to the group function $\Lambda_{(p)}$, namely,

$$\int\bar{\Lambda}_{(p)}(1,2,\cdots,p)\,\Delta_{(q)}(1,2',\cdots,N'-q')\,d\tau_1=0. \tag{8}$$

Matrix elements between strong orthogonal group

functions over one- and two-electron operators have been discussed by McWeeny[12,19] and are given here in a convenient form for further use. It is noted that in the p-correlated product of Eq. (6) the group function $\Delta_{(p)}$ is normalized whereas $\Lambda_{(p)}$ is not.

The overlap integral is

$$S_{(p)(p)'} = (\Psi_{(p)} \mid \Psi_{(p)'}) = (\Lambda_{(p)} \mid \Lambda_{(p)'}), \tag{9}$$

where $(p)'$ denotes that the detailed structure of $\Lambda_{(p)'}$ can differ from that of $\Lambda_{(p)}$, but both (p) and $(p)'$ refer to the same p-tuple $i_1, i_2, \cdots, i_p$. The one-electron matrix elements are given by

$$\begin{aligned} h_{(p)(p)'} &= (\Psi_{(p)} \mid h(\mathbf{N}) \mid \Psi_{(p)'}) \\ &= (\Lambda_{(p)} \mid h(\mathrm{p}) \mid \Lambda_{(p)'}) \\ &\quad + S_{(p)(p)'}(\Delta_{(p)} \mid h(\mathbf{N}-\mathrm{p}) \mid \Delta_{(p)}), \end{aligned} \tag{10}$$

and the two-electron matrix elements are

$$\begin{aligned} g_{(p)(p)'} &= (\Psi_{(p)} \mid g(\mathbf{N}) \mid \Psi_{(p)'}) \\ &= (\Lambda_{(p)} \mid g(\mathrm{p}) \mid \Lambda_{(p)'}) \\ &\quad + \sum_{\rho[\neq(p)]}^{N} [\Lambda_{(p)}(1, \cdots, p)\,\phi_\rho(\mathrm{p}+1) \mid g(\mathrm{p}+1) \\ &\quad - g(\mathrm{p}) \mid \left(1 - \sum_{i=1}^{p} P_{i,p+1}\right) \\ &\quad \times \Lambda_{(p)'}(1, \cdots, p)\,\phi_\rho(p+1)] \\ &\quad + S_{(p)(p)'}[\Delta_{(p)} \mid g(\mathbf{N}-\mathrm{p}) \mid \Delta_{(p)}], \end{aligned} \tag{11}$$

where P_{ij} permutes particles i and j and

$$h(\mathrm{n}) \equiv \sum_{i=1} h(i) \text{ and } g(\mathrm{n}) \equiv \sum_{i<j}^{n} g(i,j) \tag{12}$$

are one- and two-electron operators, respectively.

II. PAIR-CORRELATED GENERALIZED PRODUCT WAVEFUNCTION

A. Structure of the Total Wavefunction

The general pair-correlated group function (geminal) can be written from Eqs. (4) and (5) as

$$\begin{aligned} \Lambda_{i_1 i_2}(1,2) &= 2^{-1/2}(1 - P_{12})[\phi_{i_1}(1)\,\phi_{i_2}(2) + f_{i_1}(1)\,\phi_{i_2}(2) \\ &\quad + \phi_{i_1}(1) f_{i_2}(2) + f_{i_1 i_2}(1,2)]. \end{aligned} \tag{13}$$

Now let us introduce a complete set of orthonormal one-electron spin-orbitals from which we select a truncated set $\{\phi_n\}_1^M$ $(M \geq N)$ of spin functions for expanding the complete wavefunction. In addition we also introduce a set of pseudo-operators spanning the subspace defined by $\{\phi_n\}_1^N$. These quantities are defined by the relations,

$$P^{\rho}_{(q)} \equiv \prod_{l[\neq(q)]} (1 - \delta_{l\rho}), \tag{14}$$

and its complement

$$Q^{\rho}_{(q)} \equiv 1 - P^{\rho}_{(q)}. \tag{15}$$

The operators $P^{\mu}_{(q)}$ included in expansions of the type,

$$\begin{aligned} g(1, 2, \cdots, n) = \sum_{\mu_1, \mu_2, \cdots, \mu_n} & C_{\mu_1 \mu_2 \cdots \mu_2} \\ & \times P^{\mu_1}_{(q)} P^{\mu_2}_{(q)} \cdots P^{\mu_n}_{(q)} \\ & \times \phi_{\mu_1}(1)\,\phi_{\mu_2}(2) \cdots \phi_{\mu_n}(n), \end{aligned}$$

remove all components of $\{\phi_n\}_1^N$ except those belonging to (q). Thus one has for g the strong orthogonality condition,

$$\int \bar{\Delta}_{(q)}(1, 2 \cdots) g(1, 2' \cdots, n')\, d\tau_1 = 0. \tag{16}$$

From the definitions of Eqs. (14) and (15) it is seen that $P^{\rho}_{(q)}$ and $Q^{\rho}_{(q)}$ are idempotent and behave as true projection operators. The $P^{\rho}_{(q)}$ have the same function in the present formulation as the more general projection operators, defined by Szasz,[10] needed to ensure strong orthogonality in the sense of Eq. (8) for the general pair function. The simple form of the projection operators possible here results from the introduction of a one-electron expansion set right at the outset.

From the spin-function set $\{\phi_n\}_1^M$ and the projection operators defined by Eq. (14) the spin-orbital expansion, $\Omega_{i,j}$, of Λ_{i_1, i_2} can be written as

$$\Omega_{i,j}(1,2) = \sum_{\mu,\nu} C^{ij}_{\mu\nu} P^{\mu}_{i} P^{\nu}_{j} [\phi_\mu(1)\,\phi_\nu(2) - \phi_\mu(2)\,\phi_\nu(1)]/\sqrt{2}, \tag{17}$$

where the $C^{ij}_{\mu\nu}$ are the geminal expansion coefficients, which may be complex, and for simplicity, the subscripts i, j are used in place of i_1, i_2. The indices μ, ν take on all values $[1, M]$ such that the $C^{ij}_{\mu\nu}$ are defined for $\mu < \nu$ except that for $\nu < N+1$, $C^{ij}_{\mu\nu}$ is defined for all values $[1 \leq \mu \leq M]$. Combining Eqs. (6) and (17) one can write for the pair-correlated group products (or pair-correlated configurations)

$$\Psi_{ij} = \mathcal{A}'[\Omega_{ij}\,\Delta_{ij}]. \tag{18}$$

A pair-correlated wavefunction which includes all pair correlations must contain all such configurations. The total pair-correlated wavefunction is then a finite expansion[9,10] of pair-correlated group configurations consisting of $N(N-1)/2$ terms of the type defined by Eq. (18), and has the form

$$\Psi = \sum_{i<j} D_{ij}\,\Psi_{ij}, \tag{19}$$

where the D_{ij} are variationally determined pair-correlated group-product expansion coefficients.

The wavefunction of Eq. (19) is the generalized product analog of the CI wavefunction containing all effects through pair excitations which can be written[21] as

$$\Psi = C_0 \Phi_0 + \sum_i \sum_a C_i^a \Phi_i^a + \sum_{i<j} \sum_{a<b} C_{ij}^{ab} \Phi_{ij}^{ab}, \quad (20)$$

where i, j refer to reference state orbitals, and a, b refer to excited orbitals, and the Φ's are Slater determinants constructed via the Nesbet[22] recipe. By inserting Eq. (17) into (18) and then expanding Eq. (19) the coefficients $C_{\mu\nu}^{ij}$ and D_{ij} are easily related to the CI expansion coefficients in Eq. (20). One obtains (with μ, ν replaced by a, b, respectively, in the $C_{\mu\nu}^{ij}$)

$$C_0 = \sum_{i<j} (-1)^{i+j-1} D_{ij} C_{ij}^{ij}, \quad (21a)$$

$$C_j^a = \sum_{i(<j)} (-1)^{i+j-1} D_{ij} C_{aj}^{ij} + \sum_{i(>j)} (-1)^{i+j-1} D_{ji} C_{ja}^{ji}, \quad (21b)$$

$$C_{ij}^{ab} = (-1)^{i+j-1} D_{ij} C_{ab}^{ij}, \quad (21c)$$

where the factors $(-1)^{i+j-1}$ arise from permuting the electron labels in Eq. (18) so that they conform with the labels in Eq. (20). From Eq. (21) it is seen that the coefficients D_{ij} weight the corresponding Ψ_{ij}'s contribution to the total wavefunction, while the coefficients from Eq. (20) weight the contribution of the corresponding excited determinant to the total wavefunction.

By comparing Eq. (19) with Eq. (20) it is seen that the wavefunction in generalized product form contains more parameters than the corresponding CI wavefunction. This is more clearly seen from Eqs. (21a) and (21b) which show that several geminal expansion coefficients refer to the same state in the CI expansion. Equation (21a) shows that all the coefficients C_{ij}^{ij} refer to the reference state, so that only one parameter can be associated with them, thus one can require

$$C_{ij}^{ij} = C_{ij+1}^{ij+1} = C_{i+1,j+1}^{i+1,j+1} \quad . \quad (22)$$

From Eq. (21b) it is seen that all geminal expansion coefficients containing a common index refer to the same antisymmetrized product $(\phi_1 \phi_2 \cdots \phi_{j-1} \phi_\mu \phi_{j+1} \cdots \phi_N)$, i.e., the singly substituted product where ϕ_j has been replaced by ϕ_μ, and only one variation parameter can be associated with it, which leads to the restrictions,

$$\begin{aligned} &C_{i\mu}^{ij} - C_{i+1,\mu}^{i+1,j} = 0, \; i = 1, 2, \cdots, j-2; \; j = 2, \cdots, N, \\ &C_{j-1,\mu}^{j-1,j} - C_{\mu,j+1}^{j,j+1} = 0, \; j = 2, 3, \cdots, N-1, \\ &C_{\mu k}^{jk} - C_{\mu,k+1}^{j,k+1} = 0, \; j = 1, 2, \cdots, N-1; \\ &k = j+1, j+2, \cdots, N \end{aligned} \quad (23)$$

for all μ in the interval $[N+1, M]$. Finally it is convenient to require that the geminals are normalized, namely,

$$\int d\tau_1 \int d\tau_2 \, \bar{\Omega}_{ij}(1,2) \Omega_{ij}(1,2) = 1. \quad (24)$$

With these restrictions the number of variational parameters remaining is consistent with the CI expansion given by Eq. (20).

Two special cases arise: These are when $M = N$ and when $M = N+1$. In both cases there are not enough C^{ij}'s to satisfy Eqs. (22) and (23) and therefore restrictions must be placed on the D_{ij}'s. Finally for $M = N$ all D_{ij}'s are determined and Eq. (19) reduces to the independent particle wavefunction.

B. Energy and Variational Equations

The total electronic energy for the system can now be written in the form

$$E = (\Psi \mid \mathcal{H} \mid \Psi)/(\Psi \mid \Psi) = \mathbf{D}^\dagger \mathbf{H} \mathbf{D} / \mathbf{D}^\dagger \mathbf{S} \mathbf{D}, \quad (25)$$

where $\mathcal{H}$ is the Hamiltonian of the system, and the elements of the matrix $\mathbf{H}$ are defined by

$$H_{ij,kl} = (\Psi_{ij} \mid \mathcal{H} \mid \Psi_{kl}), \quad (26)$$

while elements of the overlap matrix $\mathbf{S}$ are given by

$$S_{ij,kl} = (\Psi_{ij} \mid \Psi_{kl}). \quad (27)$$

The elements of $\mathbf{D}$ can now be determined by requiring that E is stationary with respect to their variation, i.e.,

$$(\mathbf{H} - E\mathbf{S})\mathbf{D} = 0. \quad (28)$$

With index pairs counted according to the rule $i + (j-1)(j-2)/2$ (and similarly for kl) the $N(N-1)/2$-dimensional matrix $\mathbf{H}$ has the form

$$\mathbf{H} = \begin{bmatrix} H_{12,12} & H_{12,13} & H_{12,23} \cdots H_{12;N-1,N} \\ H_{13,12} & H_{13,13} & H_{13,23} \cdots H_{13;N-1,N} \\ H_{23,12} & H_{23,13} & H_{23,23} \cdots H_{23;N-1,N} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ H_{N-1,N;12} & H_{N-1,N;13} & H_{N-1,N;23} \cdots H_{N-1,N;N-1,N} \end{bmatrix}. \quad (29)$$

C. Matrix Elements of S and H

From Eq. (29) it is seen that the matrix elements of $\mathbf{H}$ (and of $\mathbf{S}$) can be classified into diagonal elements with two distinct indices, and off-diagonal elements with three of four distinct indices. On substituting Eq. (18) into Eqs. (26) and (27) it is observed that the diagonal elements are in strong orthogonal form and can be directly expanded with the help of Eqs. (9)–(11). On the other hand the off-diagonal elements are *not* in strong orthogonal form. Consider for example the element $H_{ij,ik}$. In this case the subspaces defined by Ω_{ij} [from the lhs of the Hamiltonian in Eq. (26)] and Δ_{ik} (from the rhs of the Hamiltonian) overlap through

the orbital ϕ_j and similarly Ω_{ik} and Δ_{ij} overlap through the orbital ϕ_k. Strong orthogonality can be restored by defining three- and four-particle groups for the three and four index elements, respectively, in such a way that the groups once again span mutually orthogonal subspaces.

For the three-particle group, let

$$\Upsilon_{ijk}(1,2,3)=\mathcal{A}(-ijk)\,\Omega_{ij}(1,2)\,\Phi_k(3), \tag{30}$$

where the first two indices of the triplet ijk refer to the geminal, and the third index to the odd orbital. The factor $(-ijk)$ is defined to be ± 1 if for $i<j<k$ the number of permutations needed to bring the electron labels into the same numerical order as the index triple is even (odd). Thus for $\Upsilon_{ikj}(1,2,3)$ one has that $(-ikj)=-1$. The four-particle group function is defined as

$$\Gamma_{ij,kl}(1,2,3,4)=\mathcal{A}\Omega_{ij}(1,2)[\phi_k(3)\,\phi_l(4)-\phi_k(4)\,\phi_l(3)]/\sqrt{2}, \tag{31}$$

where the first two indices of the quadruple refer to the geminal and the last two to the 2×2 determinant.

Using the three-particle group functions the three-index matrix elements take the form,

$$H_{ij,ik}=(\mathcal{A}'\Upsilon_{ijk}\,\Delta_{ijk}\,|\,\mathcal{H}\,|\,\mathcal{A}'\Upsilon_{ikj}\,\Delta_{ijk}), \tag{32}$$

and for the four-index matrix elements one has

$$H_{ij,kl}=(\mathcal{A}'\Gamma_{ij,kl}\,\Delta_{ijkl}\,|\,\mathcal{H}\,|\,\mathcal{A}'\Gamma_{kl,ij}\,\Delta_{ijkl}). \tag{33}$$

In this way the off-diagonal elements in the variational matrix of Eq. (29) lead to the inclusion of higher order interactions then the simple pair interactions obtained from the diagonal terms. They will be discussed later.

With the help of Eqs. (9) and (17) the matrix elements of **S** can be obtained. These are

$$S_{ij,ij}=\sum_{\mu\nu}\bar{C}^{ij}_{\mu\nu}C^{ij}_{\mu\nu}P^{\mu}_{i}P^{\nu}_{j}, \tag{34}$$

$$S_{ij,ik}=\sum_{\mu}\bar{C}^{ij}_{\mu j}C^{ik}_{\mu k}P^{\mu}_{i}, \tag{35}$$

$$S_{ij,kl}=\bar{C}^{ij}_{\mu}C^{kl}_{\mu}. \tag{36}$$

With the diagonal and off-diagonal elements of **H** expressed in the forms of Eqs. (26), (32), and (33), respectively, they can be evaluated by substitution into Eqs. (10) and (11). The resulting expressions are written in terms of one- and two-electron integrals defined by

$$(\alpha\,|\,h\,|\,\beta)=\int d\tau\,\bar{\phi}_{\alpha}(\tau)h\phi_{\beta}(\tau), \tag{37}$$

where τ represents the space-spin variables x,y,z, and s, of ϕ and

$$(\alpha\beta\,|\,\gamma\delta)=\int d\tau_1\int d\tau_2\,\bar{\phi}_{\alpha}(\tau_1)\,\phi_{\beta}(\tau_1)\,\bar{\phi}_{\gamma}(\tau_2)\,\phi_{\delta}(\tau_2)/r_{12}, \tag{38}$$

and certain matrices whose elements are functions of the geminal expansion coefficients and the pseudo-operators defined by Eq. (14).

They have the form

$$H_{ij,kl}=\sum_{\mu\mu'}\mathfrak{U}^{ij,kl}_{\mu\mu'}\{(\mu\,|\,h\,|\,\mu')+\sum_{\sigma}Q^{\sigma}_{ijkl}[(\mu\mu'\,|\,\sigma\sigma)-(\mu\sigma\,|\,\sigma\mu')]\}+\sum_{\mu\mu',\nu\nu'}\mathfrak{V}^{ij,kl}_{\mu\mu',\nu\nu'}[(\mu\mu'\,|\,\nu\nu')-(\mu\nu'\,|\,\nu\mu')], \tag{39}$$

where

$$\mathfrak{U}^{ij,kl}_{\mu\mu'}=U^{ij,kl}_{\mu\mu'}+S_{ij,kl}\,\delta_{\mu\mu'}Q^{\mu}_{ijkl} \tag{40}$$

and

$$\mathfrak{V}^{ij,kl}_{\mu\mu',\nu\nu'}=V^{ij,kl}_{\mu\mu',\nu\nu'}-\tfrac{1}{2}S_{ij,kl}\,\delta_{\mu\mu'}\,\delta_{\nu\nu'}Q^{\mu}_{ijkl}Q^{\nu}_{ijkl}. \tag{41}$$

The last terms in Eqs. (40) and (41) are due to the independent particle terms in Eqs. (10) and (11). The coefficients $U^{ij,kl}_{\mu\mu'}$ and $V^{ij,kl}_{\mu\mu',\nu\nu'}$ for the diagonal and off-diagonal terms can be written with the help of the intermediate quantities

$$\omega^{\rho}_{ij,\mu}=C^{ij}_{\rho j}P^{\rho}_{i}\delta_{i\mu}+C^{ij}_{i\rho}P^{\rho}_{j}\delta_{j\mu} \tag{42}$$

and

$$v^{\mu\nu}_{ij}=C^{ij}_{\mu\nu}\,P^{\mu}_{i}P^{\nu}_{j}-C^{ij}_{\nu\mu}\,P^{\nu}_{i}P^{\mu}_{j} \tag{43}$$

as follows:

$$U^{ij,ij}_{\mu\mu'}=\sum_{\rho}\bar{v}^{\mu\rho}_{ij}v^{\mu'\rho}_{ij}, \tag{44}$$

$$U^{ij,ik}_{\mu\mu'}=\bar{C}^{ij}_{\mu j}C^{ik}_{\mu' k}P^{\mu}_{i}P^{\mu'}_{i}-\sum_{\rho\rho'}\bar{C}^{ij}_{\rho\rho'}C^{ik}_{\rho\rho'}P^{\rho}_{i}P^{\rho'}\delta_{\mu k}\delta_{\mu' j}+\sum_{\rho}(C^{ik}_{\rho k}P^{\rho}_{i}\delta_{\mu j}\bar{v}^{\rho\mu}_{ij}+\bar{C}^{ij}_{\rho j}P^{\rho}_{i}\delta_{\mu k}v^{\rho\mu'}_{ik}) \tag{45}$$

and

$$U^{ij,kl}_{\mu\mu'}=C^{kl}_{\mu\nu}\bar{\omega}^{\mu}_{ij,\mu'}+\bar{C}^{ij}_{\mu\nu}\omega^{\mu'}_{kl,\mu}-\sum_{\rho}\bar{\omega}^{\rho}_{ij,\mu'}\omega^{\rho}_{kl,\mu}. \tag{46}$$

For the $V^{ij,kl}$ one obtains

$$V^{ij,ij}_{\mu\mu',\nu\nu'}=\bar{C}^{ij}_{\mu\nu}C^{ij}_{\mu'\nu'}P^{\mu}_{i}P^{\nu}_{j}P^{\mu'}_{i}P^{\nu'}_{j}, \tag{47}$$

$$V^{ij,ik}_{\mu\mu',\nu\nu'}=\bar{C}^{ij}_{\mu\nu}C^{ik}_{\mu' k}P^{\mu}_{i}P^{\nu}_{j}P^{\mu'}_{i}\delta_{j\nu'}+\bar{C}^{ij}_{\mu j}C^{ik}_{\mu\nu'}P^{\mu}_{i}P^{\mu'}_{i}P^{\nu'}_{k}\delta_{k\nu}+\delta_{k\nu}\delta_{j\nu'}\sum_{\rho}\bar{v}^{\rho\mu}_{ij}v^{\rho\mu'}_{ik}, \tag{48}$$

and finally

$$V^{ij,kl}_{\mu\mu',\nu\nu'}=\bar{C}^{ij}_{\mu\nu}C^{kl}_{\mu'\nu'}P^{\mu}_{i}P^{\nu}_{j}\delta_{\mu' i}\delta_{\nu' j}+\bar{C}^{ij}_{ij}C^{kl}_{\mu'\nu'}P^{\mu'}_{k}P^{\nu'}_{l}\delta_{\mu k}\delta_{\nu l}+\bar{\omega}^{\mu}_{ij,\mu'}\omega^{\nu'}_{kl,\nu}+\sum_{\rho}(\delta_{\mu' i}\delta_{\nu' j}\omega^{\rho}_{kl,\nu}\bar{v}^{\rho\mu}_{ij}+\delta_{\mu k}\delta_{\nu l}\bar{\omega}^{\rho}_{ij,\nu'}v^{\rho\mu'}_{kl})+\sum_{\rho\rho'}\bar{C}^{ij}_{\rho\rho'}C^{kl}_{\rho\rho'}P^{\rho}P^{\rho'}\delta_{\mu k}\delta_{\mu' i}\delta_{\nu l}\delta_{\nu' j}. \tag{49}$$

By use of Eqs. (34)–(36) and (39)–(49) it is possible to evaluate all the matrix elements of **S** and **H** appearing in Eq. (28) once the geminal expansion coefficients and a suitable one-electron basis have been determined.

D. The Total Wavefunction and the Independent Electron Pair Approximation (IEPA)

When the Ψ_{ij} of Eq. (18) are expanded into their CI forms with the help of Eqs. (20) and (21) one recognizes at once the IEPA wavefunctions.[9,22] The only difference between the IEPA expansions and the Ψ_{ij} is the normalization which is[22]

$$C_{ij}^{ij} = 1, \tag{50}$$

so that

$$S_{ij,ij} = 1 + \sum_{\mu} (\bar{C}_{\mu j}^{ij} C_{\mu j}^{ij} + \bar{C}_{i\mu}^{ij} C_{i\mu}^{ij}) P^{\mu} + \sum_{\mu\nu} \bar{C}_{\mu\nu}^{ij} C_{\mu\nu}^{ij} P^{\mu} P^{\nu} \geq 1. \tag{51}$$

With this change the energy expectation value for Ψ_{ij} is given by

$$E_{ij} = H_{ij,ij}/S_{ij,ij}\ , \tag{52}$$

and the coefficients are determined by requiring that E_{ij} is stationary.[23]

The IEPA method yields a pair-correlated variational wavefunction for each pair of electrons, i.e., a set of expansion coefficients $C_{\mu\nu}^{ij}$. These coefficients can be used to evaluate the off-diagonal elements of **S** and of **H**. One can then solve Eq. (28) and obtain an expectation value of the total energy and a set of pair-correlated configuration expansion coefficients. In this way a total generalized product wavefunction can be obtained from one of the IEPA's.

DISCUSSION

The requirement that the off-diagonal elements of **H** be expressed in terms of strong orthogonal group functions made it necessary to introduce three- and four-particle groups spanning an electron subspace orthogonal to the remaining one-electron Hilbert space. In that way the three- and four-particle coupling terms known to be present in the energy expression of the CI expansion also appear in a simple and obvious way in the energy expressions of the generalized product expansion of Eq. (19).

By inserting Eq. (13) into Eqs. (32) and (33) one can obtain these terms explicitly, namely $(\phi_i f_j \phi_k \mid \mathcal{H} \mid \mathcal{A} f_{ik} \phi_j)$, $(f_{ij} \phi_k \mid \mathcal{H} \mid \mathcal{A} f_{ik} \phi_j)$, and $(f_{ij} \phi_k \phi_l \mid \mathcal{H} \mid \mathcal{A} f_{kl} \phi_i \phi_j)$.[9,10,13,24] The first of these is a pseudo-three-body term and vanishes if the reference orbitals are Brueckner orbitals.[11,25] The second type is a pair–pair interaction which is expected to be small[9] while the last type can be nonnegligible for electrons located in the same region of space. Even though these terms are frequently small they have been shown to make important contributions[5,26] and indeed previous analysis has shown that the difference in correlation energy recovered between the IEPA and the pair-correlated CI expansion can be as much as 40%.[27]

The generalized product wavefunction given by Eq. (19) provides a very compact form for writing a correlated wavefunction. In comparing it with the CI wavefunction of Eq. (20) one sees that the generalized product expansion changes the emphasis somewhat in that one now considers the correlation contribution of a given pair as a whole rather than as a number of contributions from orbital excitations. On the other hand on inserting Eq. (17) into Eq. (18) and expanding, the orbital description is easily recovered. A further advantage of the generalized product wavefunction is that it provides the possibility of obtaining a variational wavefunction from the IEPA method by diagonalizing an $N(N-1)/2$-dimensional matrix in place of the much larger matrices encountered in the usual CI calculation. The importance of optimizing the geminal expansion coefficients beyond the IEPA and some applications to small systems will be reported elsewhere.

Finally it should be remarked that the method developed here can be extended to higher order correlations without any essential changes in procedure. For example, the generalized product quadruple-correlated wavefunction has the form

$$\Psi = \sum_{i<j<k<l} D_{ijkl} \Psi_{ijkl},$$

where

$$\Psi_{ijkl} = \mathcal{A}'[\Lambda_{ijkl} \Delta_{ijkl}].$$

A possible form for the four-particle group function would be an expansion in terms of spin geminals, i.e.,

$$\Lambda_{ijkl}(1, 2, 3, 4) = \sum b_{\alpha\beta\gamma\epsilon}^{ijkl} \mathcal{A}' \Lambda_{\alpha\beta}(1, 2) \Lambda_{\gamma\epsilon}(3, 4).$$

In this way another set of expansion coefficients is added, which could be variationally determined.

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